

## **Chemical Kinetic Modeling of Hydrocarbon Ignition\***

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Ignition phenomena play an enormous role in many practical combustion phenomena. The kinetics of ignition are in fact more complex and technically more demanding than the kinetics of steady combustion and flame propagation. In addition to actual hydrocarbon ignition problems, such as spark ignition in internal combustion engines, ignition is very important in pulse combustion, in shock tubes, in detonations, and in engine knock. Therefore there is considerable reason to develop reliable and general kinetic models to describe ignition under practical combustion conditions.

Hydrocarbon ignition kinetics varies dramatically according to the temperature and pressure of the system involved. At high temperatures, such as in shock tubes and detonations, the unimolecular decomposition of the fuel and of the radical species produced from the fuel are dominant. In addition, the major chain branching reaction involves the reaction of atomic H atoms with molecular oxygen. The influence of flame inhibitors and suppressors of detonations and explosions can be understood very well in terms of their effects on the rate of production and consumption of H atoms.

In contrast, at much lower temperatures, an entirely different set of elementary chemical reactions control ignition processes. These reactions include addition of molecular oxygen to alkyl radicals, followed by isomerization of the resultant radical species, and other complex reaction paths. There are many chain propagation reaction paths in this system, and the major chain branching mechanism involves the production and decomposition of various dihydroperoxide species and the production of multiple radicals. The ability of a kinetic model to describe these many reaction paths is very difficult and demanding to provide, and these processes place many close constraints upon the kinetic model. However, the response of the chemical system to slight variations in the overall rate of chain branching is so sensitive that experimental ignition data can provide very detailed information on many of these reaction paths.

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In this paper and presentation, differences in ignition kinetics for hydrocarbon fuels at different temperatures and pressures are detailed. Influences of fuel molecule size, structure, and other elements are described, all of which affect the rate of ignition, detonability, knock tendency, cetane number in diesel engines, and other practical combustion properties. Strategies for modifying these ignition rates, and their applications to practical systems, will be discussed for both chemical and physical variables. The needs for theoretical chemical physics and quantum mechanical information to describe these practical fuels will be emphasized.